THE HOT AND COLD OF RECYCLED WATER IN REFINERIES

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Abstract

Refineries in southern California have been successfully using recycled water, specifically Title-22 water, in their cooling towers and as boiler feed water. The use of recycled water, from the customers' perspective, can have both energy and reliability benefits. The energy benefits are primarily associated with avoiding on-site treatment. The reliability benefits arise from using a supply of water that is not subject to rationing during a declared drought.

There are several factors, which affect the economic benefits of Title-22 water. One factor is the recycled water quality. The Title-22 water contains some additional minerals, which require chemical treatment, such as pH control, to prevent mineral deposits. Other minerals act as corrosion inhibitors, prolonging the cooling tower and boiler feed life span.

This study examines the Title-22 water and potable water data from the refineries. Included in this data are water quality parameters, such as minerals, and associated control measures or benefits; recycled water conditioning or purification processes required, whether on- or off-site, including micro-filtration, reverse osmosis, softening, and others as needed; and all monitoring required on the refinery site to assess the level of water alterations needed for both Title-22 or potable water.

The results of this study summarize the past experience of refineries which have converted from potable water to Title-22 water use in cooling towers and boiler feed water and present a cost comparison of potable water use and the conversion to and use of Title-22 water.

Introduction

The West Basin and Central Basin Municipal Water Districts (WBMWD and CBMWD) provide water to more than thirty city water departments and water companies in the Greater Los Angeles metropolitan area. Since freshwater is a most valuable resource in southern California, the W&CBMWD have undertaken a major program to make more water available by intercepting wastewater treated to secondary treatment standards before it is discharged into the ocean and further treating it to tertiary standards. CBMWD distributes recycled water from the County Sanitation Districts of Los Angeles County. Known as the recycling project, these combined programs treat and recycle 31,300 acre-feet/year (10.2 billion gallons/year) of wastewater for a variety of uses such as industrial cooling and boiler water makeup (a major user), landscape irrigation at golf courses, public parks, schools, cemeteries, and highway and road medians (a minor user), and for re-injection to replenish groundwater (a major need); all to replace freshwater which will be available for drinking (i.e., potable) water use.

Background

There are several factors that led to the conversion from potable water use to recycled water use. The crude oil refining industry in the Los Angeles area was historically and continues to be the largest user of freshwater, primarily for process cooling and boiler makeup. By switching to recycled water, particularly for the plant process cooling systems, these refineries significantly reduced their reliance on freshwater. In addition, a number of the refineries are geographically clustered in a few industrial areas so that distribution of Title 22 water via "purple" pipelines was both practical and economical.

Prior to complete system conversion to recycled water in cooling towers and for boiler feed, differences in freshwater and recycled water qualities were thoroughly evaluated. Recycled water quality and site-specific considerations such as refinery design, materials of construction and operating characteristics, along with the proper water treatment chemistry, strongly influenced the potential for successful use of recycled water. Therefore, it is important for each user and potential user of recycled water to thoroughly examine and evaluate the possible effects of recycled water on equipment protection and life expectancy relative to water-related corrosion, scaling, deposition, and biofouling. A study of the associated changes and costs required in cooling water treatment can identify the important factors that should be considered when switching from freshwater to recycled water. Puckorius & Associates, Inc., completed a detailed study by mid-1994 on the impact of the recycled water and chemical water treatment requirements that would enable the use of recycled water as the only external source of makeup for all of a refinery's cooling and boiler systems.

The WBMWD water-recycling project receives effluent from Hyperion, the City of Los Angeles's wastewater treatment plant for further processing (flocculation & filtration or microfiltration & Reverse osmosis, then disinfection with chlorine) producing a recycled water quality consistent with criteria established by the California Department of Health Services in Administrative Code Title 22. For this reason, the recycled water from the WBMWD recycling project is frequently referred to as "Title 22 Water."

Recycled water can be successfully utilized in refinery cooling water systems. Technically, the success of the recycled water program for refinery process cooling depends upon a number of factors particular to both refineries in general and to each individual refinery. In general, these factors can be classified as:

1. Cooling system design/operating characteristics;
2. Cooling water treatment; and
3. Recycled water quality.

These three general factors are critical to successfully using recycled water as makeup to recirculated cooling water systems in refineries. The focus is on the possible effects on refinery equipment relative to corrosion, scaling, and biofouling, as well as the associated changes required in water treatment. Makeup water for boilers is produced from Title 22 water, but further refinement or purification is needed to raise the quality of the water to the standards consistent with the operating pressures and the design of the boiler systems to be treated.

Refinery Equipment and Chemical Treatment

Petroleum refineries are complex chemical processing plants that often have a variety of unit operations, steps that invariably involve heating by steam and cooling by water. Hence, water is an extremely valuable resource for refineries and used in large volumes.

Open recirculating cooling systems are the most common approach to process cooling in refineries, making heat exchangers and cooling towers the critical equipment components. These systems employ evaporative cooling towers, which use huge quantities of water. The dissolved minerals, which concentrate in the cooling water as a result of the evaporation process, impact the scaling, corrosion, and microbiological activity within the heat exchangers and cooling tower.

Chemical treatment of refinery cooling water is designed to: ensure adequate, reliable, continuous, efficient heat transfer in system heat exchangers and cooling towers; and maintain and maximize the life expectancy of all equipment in contact with the water.

Treatment of refinery boiler makeup water is designed to: ensure maximum and reliable fuel to steam thermal efficiency; and maintain and maximize the life expectancy and efficiencies of the pre-boiler, and post-boiler systems as well as the boilers themselves.

In so doing, chemical treatment must prevent or mitigate corrosion and deposition (including scaling, fouling, and microbiological activity) where water contacts metal surfaces. Although the precise chemical treatment programs for a particular refinery cooling and boiler systems is heavily dependent upon the system’s design and operating characteristics and any site-specific environmental constraints, certain generalizations can be made regarding the importance of makeup water quality and the associated treatment requirements for corrosion and deposition control.

Makeup Water Quality

A typical cooling system makeup water quality analysis can provide substantial information regarding potential corrosion and deposition problems. Typically, the parameters of primary concern are total and calcium hardness, alkalinity, silica and total suspended solids. In special situations, a number of other parameters may be important, including ammonia, phosphate, iron, total dissolved solids, organics, heavy metals, and microorganisms. Consistent quality of makeup water is an important consideration. If substantial quality variations occur, the required water treatment and water control become very difficult to maintain and thus adversely impact the system protection. Uniform water quality achieved by recycled water treatment plants is very beneficial, even essential to successful refinery utility operations.

The use of groundwater from wells on refinery property is usually restricted due to salt-water intrusion of freshwater aquifers and state, county or local extraction fees and use/purpose restrictions. These conditions have resulted in a decline or discontinuation of well water use in several refineries.

Table 1. Typical Refinery Potable Water Quality in Southern California

Constituent	Annual Average in mg/l
TDS	700
Calcium ($CaCO_3$)	118
Total Hardness	205
Total Alkalinity	160
Silica (SiO_2)	25
Ammonia (NH_3)	0.0
Total Phosphate (PO_4)	0.0

Makeup Water Quality for Evaporative Cooling Water Systems

Cooling tower water utilizing the typical southern California refinery potable water shown in Table 1 is normally limited and controlled at 4 to 5 cycles of concentration due to calcium hardness and silica solubilities, and can be used with conventional chemical treatment. Also, the somewhat high total alkalinity,160 mg/l, usually requires the use of a strong acid, such as concentrated sulfuric acid. Controlling the cycled water's pH to 7.5 ± 0.5 would require approximately 150 mg/l of 66◦ Baume sulfuric acid to minimize scaling. The corrosion, deposit, and microbiological treatment costs vary with the specific chemistry of the treatment program utilized, the cycles carried in the cooling tower systems, cooling equipment design and operating characteristics, and especially the temperatures and heat transfer rates of the numerous heat exchangers in the refinery.

Makeup Water Quality for Boiler Water Systems

Depending upon the boiler pressure, potable water typically requires either ion exchange softening or demineralization and/or reverse osmosis (RO) treatment before it can be used in boilers. The cycles of concentration that are carried usually range from five to ten for low pressure steam and 30 to 100 or more for high pressure power boilers, depending on the final feedwater (makeup plus condensate returns) quality, and steam quality requirements. Boiler water treatment and related costs depend upon the same criteria as cooling water systems, but acceptable boiler makeup water quality is much more restrictive.

Recycled Water Quality

From a technical perspective, the suitability of using recycled water as makeup to refinery cooling water systems is a function of the recycled water quality relative to the cooling system design and operating characteristics.

With respect to the cooling water parameters typically of interest, the recycled water quality versus the current imported water to all refineries is relatively good. Specifically, the hardness, alkalinity, silica, total dissolved and suspended solids levels, are comparable for recycled water quality and imported water quality for the assumed cycles of concentration, five.

However, recycled water also has some unique characteristics that significantly influence its use as makeup to refinery cooling systems. Four additional components, normally of secondary interest in potable water, are of special importance in recycled water use. They are ammonia, phosphate, chloride, and oxygen demand (COD and BOD).

Ammonia

Ammonia is a nutrient for many microorganisms and, therefore, will promote microbiological activity and biofilm or biomass growth in both the process heat exchangers and cooling tower (splash or film) fill. In addition, ammonia is extremely corrosive to copper alloys used in many refinery heat exchangers

Phosphate

The phosphate concentration in the recycled water averages 4.5 mg/l (as PO_4). Thus, at five cycles, the total concentration would be 22.5 mg/l. By operating the cooling water at a near neutral pH (7.0 – 7.5) and maintaining a sufficient dispersant level, the deposits caused by phosphate can be controlled. However phosphate will provide suitable mild steel corrosion protection.

Chloride

Dissolved chloride has a corrosive reaction with most metals. Chloride increases the general corrosion and possibly localized (pitting) corrosion. For chloride concentrations over 1,000 mg/l, mild steel should provide satisfactory service, provided the chloride does not become further concentrated under deposits on the steel surface. A chloride limit of 300 mg/l in the recirculated cooling water is often used when stainless steel equipment is involved. However, much higher levels can be tolerated unless deposits or crevices cause chloride concentration.

Oxygen Demand

Oxygen demand and organic carbon concentrations, as indicated by COD and TOC are a concern primarily because they reflect the organic content and the associated demand for oxidizing biocides used to obtain effective biofouling control in cooling systems. Levels of COD at 40 mg/l or less in makeup water are not excessive and can be effectively controlled even at 5 cycles.

Table 2. West Basin Water Reclamation Plant Title 22 Product Water

Constituent	Annual Average	Monthly Minimum	Monthly Maximum
	mg/l	mg/l	mg/l
TDS	689	600	730
pH	7.2	7.0	7.3
Calcium ($CaCO_3$)	115	97	135
Total Hardness	196	163	221
Nitrate (NO_3)	4.8	2.6	9.2
Ammonia (NH_3)	37.2	30	43
Total Phosphate (PO_4)	6.3	5.0	8.3
Ortho Phosphate (PO_4)	6.2	5.0	7.7
Total Alkalinity	280	251	301
COD	36	30	41
Iron (Fe)	0.42	0.27	0.55
Silica (SiO_2)	23	19	25
Chloride (Cl)	169	137	198
Sulphate (SO_4)	117	101	130
TOC	11	8	13
TSS	1	<1	4

The following table shows Title 22 water quality after nitrification and is typical makeup for Southern California area refineries cooling tower systems.

Table 3. West Basin Nitrification Plant Effluent

Constituent	Weekly Average	Weekly Minimum	Weekly Maximum
	mg/l	mg/l	mg/l
TDS	800	600	860
pH	7.0	6.3	7.5
Calcium ($CaCO_3$)	105	90	120
Total Hardness	185	155	195
Total Alkalinity	64.7	22.0	93.0
Nitrate (NO_3)	134	115	152
Ammonia (NH_3)	0.00	0.00	0.15
Total Phosphate (PO_4)	5.9	2.8	8.8
COD	30	21	61
Silica (SiO_2)	21	18	24
TOC	8.7	7.3	10.
TSS	5	2	12

Recycled Water Quality after Nitrification

Nitrified recycled water for the Southern California refineries has quality similar to that of potable water with several major exceptions. These exceptions considerably impact the required corrosion, deposit, and microbiological treatments needed to protect the refinery equipment in contact with cooling water.

Makeup Water Quality for Cooling Water Systems

The cycles of concentration that can be carried are 4 to 5, this is due to the similar high levels of silica in both potable and nitrified recycled water, 25 mg/l and 21 mg/l respectively. The presence of nitrates due to nitrification (ammonia converted to nitrates) and phosphate are valuable mild steel corrosion inhibitors.

In addition, nitrification produces makeup water with much lower total alkalinity (160 mg/l in potable water but only 63 mg/l in nitrified water). This greatly reduces and potentially eliminates acid requirements.

The presence of phosphate and nitrates, however, can increase microbiological treatment costs. Recycled water has 1.0 to 3.0 mg/l of residual chlorine, which can also significantly reduce microbiological treatment requirements in the cooling systems. As Phosphate concentrations in Title 22 water are gradually declining with reduced use of phosphate-based detergents. As phosphate levels in the nitrified water decrease, calcium phosphate deposition becomes easier and less costly to control.

Makeup Water Quality for Boiler Water Systems

Both potable and Title 22 water require similar purification processes and chemical treatment to be acceptable as boiler makeup. Demineralization by RO or ion exchange or both are typically used to improve Title 22 water to boiler makeup standards. In Case History No.1 RO permeate is used without additional purification. Single pass RO permeate is suitable for low-pressure boilers; Double pass RO permeate is pure enough to be used in high-pressure power boilers. See the table below for RO permeate quality.

Table 4. West Basin Boiler Feed – Single Pass Reverse Osmosis Permeate

Constituent	Weekly Average	Weekly Minimum	Weekly Maximum
	mg/l	mg/l	mg/l
TDS	26	20	46
pH	7.2	6.8	7.5
Total Hardness	0.23	0.15	0.52
Total Alkalinity	15	8	20
Nitrate (NO_3)	0.0	0.0	0.4
Ammonia (NH_3)	2.3	1.3	2.9
Total Phosphate (PO_4)	0.0	0.0	0.0
TOC	0.0	0.0	0.0
Silica (SiO_2)	0.12	0.09	0.16
TSS	0	0	2
Total Chlorine	0.0	0.0	0.0
Free Chlorine	0.0	0.0	0.3

Water Costs – Potable and Recycled Water

Title 22 water costs for nitrified, un-nitrified and RO permeates have varied due to treatment methods, delivery costs, and volumes utilized.

Water rates for refineries vary of course, but listed below are typical unit costs for potable water, Title 22 water and Title 22 water "products", including nitrified Title 22, single pass RO and double pass RO.

Water Quality	Typical Unit Cost
Potable	$580 per AF
Title 22	$223 per AF
Nitrified Title 22	$283 per AF
Single Pass RO	$549 per AF
Double pass RO	$725 per AF

Overall water costs for the refineries are significantly lower when Title 22 water is used. A significant portion of the cost difference between potable water and Title 22 water offsets the costs for supplementary chemical treatment and the chemical treatment service program management. However, there are numerous salient ancillary benefits too:

- Lower bulk chemical requirements for salt, acid, caustic soda, etc.
- Lower operations and maintenance costs
- Fewer and lower cost repairs
- Avoidance of premature system turnarounds or equipment replacement
- Reduced pumping costs
- Reduced energy requirements
- Improved quality control
- Higher thermal efficiencies
- Water supply reliability

These are real benefits that have not only contributed significant economic advantage to the refineries using Title 22 water; they have also permitted the redirection of invaluable potable water resources to further residential and commercial development.

Case Histories

The following case histories illustrate the favorable economics of water conservation and wastewater reclamation and reuse by the refining industry in Southern California.

Case History #1

Case history 1 petroleum refinery complex, located in Southern California, has been utilizing WBMWD nitrified Title 22 water since 1995 in its cooling tower systems. The use of RO permeates for boiler makeup water was added in 2001.

Table 5. Approximate Freshwater Savings Through 2003

	Year Start	Gallons per Minute	Gallons per Day	Gallons per Year	Acre Feet per Year	Total Gallons	Total Acre Feet
Cooling Tower Makeup	**1995**	**5,000**	**7.2 million**	**2.6 billion**	**6,500**	**21 billion**	**47,600**
Boiler Water Makeup	**2001**	**2,200**	**3.2 million**	**1.2 billion**	**3,400**	**2.4 billion**	**6,500**

Results of Change toTitle 22 Water for Cooling Systems Makeup

Makeup Water: Nitrified Title 22 water
Cycles of Concentration: 4-6 (same as freshwater)
Water cost savings annually: Approximately $2.3 million
Water treatment cost savings annually: Approximately 15%
Cooling Systems Operation: Overall Improvement

These results are much superior to the original cost estimates projected in 1995. The improved economics of the refinery cooling water systems operations is due in part to:

- lower phosphate levels in the reclaimed wastewater from Hyperion;
- Improved water treatment technologies, especially polymer synthesis and microbiological control techniques; and
- The increasing cost and reduced availability of potable water.

Results of Change to RO Permeate for Boiler Makeup

Makeup Water: RO permeate (from Title 22 water)
Pretreatment: Previously sodium cycle ion exchange for low and medium pressure boilers; on-site demineralized RO permeate by outsource contractor
Cycles: Previously 8 t0 10 cycles of concentration; presently 50 cycles of concentration or more
Water cost savings annually: Approximately 10%

Energy Savings: 80% to 90% (These percentages compute to several millions of dollars per year.)
Water treatment cost savings annually: Approximately 75%
Boiler equipment protection and maintenance: Near optimum

CASE HISTORY #2

Case history 2 petroleum refinery complex, located in Southern California, has been utilizing WBMWD nitrified Title 22 water since 1996 in its cooling tower systems. Initially, considerable review of other local refinery experiences with recycled water resulted in a detailed study of this refinery's cooling and boiler water systems, water use, and water requirements. The result of this study prompted the refinery to request that both nitrified Title 22 water and RO-treated nitrified Title 22 water be provided, if possible. WBMWD proceeded to evaluate this possibility and agreed to supply both water qualities. Nitrified Title 22 water supply began in 1999 and RO treated Title 22 water in 2000. The refinery chose to blend 85% R.O. permeate with 15% nitrified Title 22 water to obtain a Title 22 water product that was of excellent quality.

Table 6. Approximate Freshwater Savings Through 2003

	Year Start	Gallons per Minute	Gallons per Day	Gallons per Year	Acre Feet per Year	Total Gallons	Acre Feet
Nitrified T22 Makeup	**1999**	**2,080**	**3.0 million**	**1.0 billion**	**3,000**	**4.0 billion**	**29,000**
RO Permeate Makeup	**2000**	**2,200**	**3.2 million**	**1.2 billion**	**3,400**	**3.6 billion**	**19,500**

Results of Change to Title 22 Water for Cooling System Make-up

Makeup Water: 30% well water blended with a 70% Mixture of:

- 85% RO
- 15% Nitrified Title 22

Cycles: 10 to 14 versus 4-5 for freshwater
Potable Water savings annually: Approximately 6,400 AF
Water treatment cost savings annually: Approximately 40%
Cooling Systems Operations: Greatly improved – excellent

Table 7. West Basin Carson Regional Plant Cooling Tower Makeup
85% R.O., 15% nitrified

Constituent	Annual Average	Monthly Minimum	Monthly Maximum
	mg/l	mg/l	mg/l
TDS	140	137	145
pH	7.1	7.0	7.3
Total Hardness	32	24	40
Total Alkalinity	40	35	45
Nitrate (NO_3)	20	18	24
Ammonia (NH_3)	0.20	0.05	0.40
Total Phosphate (PO_4)	1.0	0.3	1.3
TOC	1.2	0.6	1.5
Silica (SiO_2)	3.8	2.8	5.0
TSS	1.0	0.0	1.2
Total Chlorine	1.5	1.0	2.5
Free Chlorine	0.5	0.3	1.0

This high quality makeup water permitted cooling water cycles to be raised from 4 to 5 with freshwater to 10 to 14 with recycled water. This in turn provided greater water savings by reducing blowdown requirements by over 80%. Water treatment costs were reduced by over 85% compared to that for freshwater. This is due to higher water quality and the subsequent need for lower chemical treatment use to control corrosion, deposits, and microbiological growth.

Cooling water equipment protection has also improved, resulting in more efficient operation as well as an estimated increase in life expectancy by 100%. This is a major cost savings for the refinery. Water treatment monitoring has improved to assure consistently good water chemistry.

Table 8. West Basin Carson Regional – Reverse Osmosis Permeate (Effluent) 2000

Constituent	Weekly Average	Weekly Minimum	Weekly Maximum
	mg/l	mg/l	mg/l
TDS	25	10	44
pH	7.0	6.8	7.1
Total Hardness	2.00	0.21	5.18
Total Alkalinity	20	15	25
Nitrate (NO_3)	1.0	0.6	1.3
Ammonia (NH_3)	1.9	1.2	2.9
Total Phosphate (PO_4)	0.5	0.2	0.8
TOC	0.0	0.0	0.0
Silica (SiO_2)	0.36	0.17	0.72
TSS	0.0	0.0	0.0
Total Chlorine	0.0	0.0	0.0
Free Chlorine	0.0	0.0	0.0

Table 9. West Basin Carson Regional-Nitrification Plant Effluent

Constituent	Weekly Average	Weekly Minimum	Weekly Maximum
	mg/l	mg/l	mg/l
TDS	800	600	860
pH	7.0	6.3	7.5
Calcium ($CaCO_3$)	105	90	120
Total Hardness	185	155	195
Total Alkalinity	64.7	22.0	93.0
Nitrate (NO_3)	134	115	152
Ammonia (NH_3)	0.00	0.00	0.15
Total Phosphate (PO_4)	5.9	2.8	8.8
COD	30	21	61
Silica (SiO_2)	21	18	24
TOC	8.7	7.3	10.
TSS	5	2	12

CASE HISTORY #3

Case history 3 petroleum refinery complex, located in Southern California, has been utilizing WBMWD nitrified Title 22 water since 1996 in its cooling towers. Use of Title 22 RO permeate for roughing demineralizer feedwater for boiler makeup was added in 2000.

Table 10. Approximate Freshwater Savings Through 2003

	Year Start	Gallons per Minute	Gallons per Day	Gallons per Year	Acre Feet per Year	Total Gallons	Total Acre Feet
Cooling Tower Makeup	**1996**	**2,500**	**3.6 million**	**1.3 billion**	**3,250**	**10.5 billion**	**23,800**
Boiler (Demin.) Makeup	**2001**	**1,100**	**1.6 million**	**0.6 billion**	**1,700**	**1.2 billion**	**3,250**

Results of Change toTitle 22 Water for Cooling Systems Makeup

Makeup Water: Nitrified Title 22 water
Cycles of Concentration: 4-6 (same as freshwater)
Potable Water savings annually: Approximately 4,950 AF
Water treatment cost savings annually: Approximately 15%
Cooling Systems Operation: Overall Improvement

These results are much superior to the original cost estimates projected in 1995. The improved economics of the refinery cooling water systems operations is due in part to:

- lower phosphate levels in the reclaimed wastewater from Hyperion;
- Improved water treatment technologies, especially polymer synthesis and microbiological control techniques; and

- The increasing cost and reduced availability of potable water.

Results of Change to Title 22 RO Permeate for Demineralizer Feedwater (Boiler Make-up)

Makeup Water: Demineralized RO permeate (from Title 22 water)

Pretreatment: Previously demineralized RO permeate from equipment system leased from outsourced supplier

Cycles: Same as previously, but with demineralized makeup produced with fewer demineralizer regenerations

Water cost savings annually: Approximately 40%

Boiler equipment protection and maintenance: No change

Conclusions

Petroleum refineries utilizing recycled water in the Greater Los Angeles Area have obtained major benefits when supplied by WBMWD recycled water facilities.

Savings associated with water, water treatment, energy, and improved equipment protection can add up to major cost reductions by using recycled water versus freshwater-. However, the greatest benefit has been the saving of freshwater for domestic and commercial use.

Petroleum refineries, chemical plants, power plants, and industries of all types are good candidates for recycled water use replacing freshwater use. Makeup water for cooling tower and boiler water systems are ideal uses for recycled, nitrified recycled, and RO recycled water.

West and Central Basin Municipal Water Districts are ready to assist other petroleum refineries, chemical plants, and other commercial-industrial users of freshwater to take advantage of the many benefits from utilizing recycled water. Saving freshwater by facilitating the use of “used” water is our goal.